Photoinduced Electron Transfer in Ordered Macromolecular Assemblies

FINAL REPORT
May 1, 1988 – June 30, 2002

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DISCLAIMER

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Introduction

This final report summarizes investigations completed under DOE sponsorship for the indicated grant period. The report includes brief summations of important results, a chronological listing of papers that issued from the research, and listings of selected presentations and doctoral dissertation activity. The latest results are presented in more detail in Part I. The other three parts follow and are summarized more briefly.

Part I June 1, 1997 - June 30, 2002

Helix-Forming Pyrene-Labeled Polypeptides. Aggregation of Chromophores and Other Aspects of Self Assembly.

An important theme that is struck in the most recent studies is that much is to be learned by investigation of the non-covalent self assembly of the active elements for light induced charge separation. For mimics of photosynthetic reaction centers, a priority should be placed on this critical structural feature of the natural system (e.g., motifs of scaffolding, the energetics of non-covalent binding, the development of vectorial arrays).

Investigations continued during the grant period on synthetic peptides that are capable of non-covalent assembly. With the appropriate design of amino acid sequences in these systems, vectorial arrays of helix or helix 'bundle' structures provide scaffolding for organizing photoactive elements, including chromophores and electron donor-acceptor sub-units. The synthetic polypeptides are also appealing in that strings of amino acids can be prepared with an exact primary sequence that incorporates the appropriate design elements (and with the introduction of non-native residues) using solid phase synthesis. For example, peptides consisting of 24 amino acid residues, laden with a pyrene chromophore at the N-terminus, were prepared and characterized using fluorescence and ultracentrifugation techniques. The *de novo* synthesis incorporates hydrophobic and hydrophilic residues in ordered arrays designed to induce folds of peptide chains into helix structures and to

promote peptide aggregation (formation of coiled coils). Circumstances were established under which long range electron transfer occurs between pyrene 'special pair' chromophores at N-termini and a remotely positioned electroactive residue (a tryptophan at position-9). This unique peptide bundle system (ref 34) *was the first to show high-order aggregation to form a synthetic protein of some size and to demonstrate multiple-step long range electron transfer.* To investigate the driving forces that control self assembly, the contribution of chromophore aggregation was dissected using an NMR technique (i.e., quantifying the favorable hydrophobic interaction that leads to chromophore dimer formation (ref 36). A combination of fluorescence and circular dichroism probes allowed the determination of binding constants for dimerization of two helices, with and without chromophore participation. This factorization of the free energy of binding of the photoactive peptide dimer (Figure 1) led to the conclusion that chromophore interaction between peptide units provides a significant component for stabilization of a particular twin-helix structure (in the present case, about one third of a total driving force for peptide assembly of ca. 10 kcal/mol) (ref 37).

Additional studies have been completed that contribute to our understanding of the synthetic peptide model systems. Several peptides having the same photoactive components (e.g., pyrene or oxopyrene chromophores), which depend on electrostatic contacts for additional stabilization and avoid the intervention of higher order aggregates, have been prepared and their coiling-aggregation properties characterized. For these homo- and heterodimeric polypeptides (32-residue, twin helix motifs), it was possible to show long range electron transfer that extended over 15 residues of separation of the chromophore pair and an electron donor moiety (an asparagine residue was modified by attachment of a carbazole donor unit). The data were interpreted in terms of a required participation by the hydrogen bonding network of the helix scaffold that permits electronic coupling between distant pyrene and carbazole components (ref 40). In another related study, a 32-residue peptide was induced to fold and to aggregate, resulting in the twin helix coiled coil in water with the assistance of an additive, the surfactant, SDS, at a prescribed premicellar concentration. Oxopyrene chromophores which labeled the N-terminus of this peptide underwent intra-pair electron transfer on laser flash photolysis. The conditions were defined in this study under which photoinduced charge separation can occur between two identical species that are pi stacked and reside in a protein-like environment (ref 41). A review article was prepared that summarizes work on electron transfer in helical polypeptides (ref 46)

Electron Donor-Acceptor Conjugates: Photochemistry in Unusual Media

In continuing efforts to provide systems that display long-lived charge separation in linked electron donor-acceptor structures, we have studied several different motifs of assembly and investigated to what extent unusual media play a role in controlling electron transfer rates. Among the subjects of these studies was a pyrene-based linkage that deployed the amino acid, tryptophan, as an electroactive group and a pyrene derivative as chromophore-acceptor, with alanine acting as spacer. For this system we showed that host-guest complexation of the pyrene sub-unit in the toroid-shaped cyclodextrin interior gave rise to a reduction in electron transfer rates by as much as a factor of five. NMR data provided clues as to the way in which the pyrene and Trp units were located in the cup-shape cyclodextrin guest environment (ref 39).

In another study, the chromophore, naphthalimide (NP), conjugated with the natural polyamine, spermine, was shown to undergo dimerization in several polar solvents including water. On flash photolysis, the dimers gave rise to naphthalimide radical-ions via an intra-pair electron transfer; this phenomenon was investigated in terms of the driving force necessary for reaction within the dimer to occur. The NP-spermine conjugate was also shown to self assemble in the presence of low concentrations of a polyelectrolyte of opposite charge, and photoinduced electron transfer for the resulting electrostatic complexes was also observed (ref 43). A companion study utilized a linkage of a coumarin dye framework with azole units that could be investigated in different states of protonation. This system was used to probe, via dye-polymer self assembly, the pH dependent conformational transition for the polymer electrolyte (poly(methacrylic acid), PMAA) in which a charged elongated random coil collapses to a neutralized cluster (similar to a globular protein).

Two studies involved the well known xanthene dye, rhodamine 6G (R6G) under different conditions of laser photolysis. As part of a collaborative effort with a Notre Dame Radiation Laboratory group (P. V. Kamat), R6G incorporated onto gold nanoparticles, was shown to form large metal-dye clusters (e.g., 20-30 nanometer dimensions) under strong laser excitation in the visible. The results were interpreted (ref 35) in terms of neutralization of Au surface charges by dye counter-ions, allowing gold cluster formation and further growth of particles upon laser excitation

via an internal heating-melting-fusion mechanism. A second study of R6G focused on photoinduced electron transfer for the dye, when it is ion-paired in a low polarity medium. This project was devoted to determining the quantum efficiency of a process in which pairs of ions (e.g., R6G+, SCN-) under excitation give rise to neutral radicals that escape solvent cages and show effective long lived charge recombination. The rhodamine thiocyanate combination proved effective for this strategy, giving rise to 10-20% efficiency of high energy radicals on laser photolysis in the visible (532 nm) (ref 44).

A promising avenue for future investigations is indicated in our most recent study of conjugates of the acridinium ion (Ac) with various electron donor species. The current effort is focused on linkage of oligomers of thiophene (Th). Electron transfer between Ac and Th units have been observed for the new compounds that incorporate one, to as many as six, thiophene units (e.g., A5T6, Figure 2). These large arrays give rise to high yields of charge separation (i.e., charge shift to the Th sub-unit) that can be observed in solution and in a solid matrix of sucrose octaacetate at room temperature (poster).
(Refs 32 – 46)

Part II June 1, 1988 – May 31, 1991

Most of the reported work has to do with organic polymers or biopolymers (particularly synthetic peptides) that have been modified by covalent attachment (or other means of binding) of organic chromophores and electron transfer agents. Specific projects involve (1) peptide conjugates bearing electroactive residues such as tryptophan and specifically labeled at the N- or C-terminus of peptide chains; (2) the electrostatic binding of organic dyes to poly- electrolytes (polyacrylates) for which the formation of dimeric aggregates of bound dye that display unusual photophysical and electron transfer properties is important; (3) a study of the binding of dyes and electron transfer agents to the "protein mimic", polyvinyl-2-pyrrolidinone (PVP), in hydrophobic domains that depend on specific H-bond interaction; and (4) completion of an earlier study having to do with the triplet state properties of charge-transfer (CT) complexes of a high potential quinone and various electron donors [investigation of the properties of triplet (contact) radical-ion pairs].
(Refs 1 – 8)

Part III May 1, 1991 –May 31, 1994

Investigations carried out in our laboratory during the report period focused on photochemical properties of organic polymers or synthetic peptides that have been modified by covalent attachment (or other means of binding) of organic chromophores and electron transfer agents. Specific projects involved:

(1) reversible photoinduced electron transfer for amino acid or peptide derivatives (conjugates) bearing the electroactive residue, tryptophan (Trp), and specifically labeled at the N- or C-terminus of peptide chains with non-native photoactive components;

(2) elucidation of intramolecular hole or electron transfer processes involving conjugates of the xanthene dye, eosin and peptides containing Trp or tyrosine (Tyr), both in solvents and in microdomains of the polymer, poly(vinyl-2-pyrrolidinone) (PVP);

(3) the photophysical properties of cationic organic dyes bound to polyelectrolytes (polyacrylates), either through hydrophobic attraction to the globular (largely uncharged) forms of the polymers, or through aggregation of dye (bound dimers) with polymers in their charged (random coil) form ;

(4) study of circular dichroism (CD) and other photophysical properties associated with electrostatic complexes of cationic dyes and the peptide electrolyte, poly(L)glutamic acid (PLGL) where self-assembly of helix structures is important;

(5) synthesis of acridinium dyes with twisted single-bond linkages to electron donors; flash kinetic investigation has demonstrated the importance of a reversible charge shift (CSH) reaction that is tunable in terms of decay times for the charge separated state;

(6) photochemical electron transfer involving a "catalytic triad" of a polypeptide (poly-L-histidine), having (a) electrostatic binding sites. (b) radical-ion-trapping nucleophilic sites, and (c) covalent attachment of a quinone that serves as an electron transfer sensitizer; the peptide serves as a template for two-electron oxidation of a heterocyclic sulfide (a thianthrene derivative) to its sulfoxide.

The principal interest in these systems concerns the influences of the structures of polymers/peptides in the control over proximity, spacial dimensions, and organization of photoactive electron donors and acceptors. Also important is the deployment of various linkages that utilize organic functional groups (some with unusual geometries) as spacers or "conduits" for long-range electron transfer (LRET). The well-ordered secondary structures (e.g., the alpha-helices) adopted by peptide polymers, and the capabilities for synthetic modification of peptide side

chains and end groups with chromophores or electroactive substituents provide another focal point. Part of the longer range effort focuses on polypeptides that can be fashioned in such a way as to hold reactive groups in a reasonably predictable proximity and further provide opportunities for self-assembly of "reaction centers" having vectorial properties, for charge entrainment or multiple electron transfers.

(Refs 9 – 20)

Part IV June 1, 1994 – May 31, 1997

Investigations carried out during this grant period include (1) time resolution of electron transfer events in the fs/ps time domain for polypeptide oligomers have end-to-end charge separation; (2) FT-ESR/CIDEP, and (3) peptide conformational analysis (NMR). Specific projects as follows:

(1) Synthesis of amphipathic helices for the construction of *de novo* reaction centers (synthetic proteins equipped with chromophores and redox agents)

(2) Characterization of peptide oligomers capable of end-to-end electron transfer across 1-3 amino acid spacer residues: charge transfer interactions and ps time scale electron transfer through peptide bonds; defining the role of aromatic amino acid side chain substitution

(3) Preparation of acridinium dye derivatives containing various electron donor groups with particular attention to the reducing group, thianthrene; fs/ps study of multistep electron transfer for dyad and triad arrays

(4) Study of cationic dye binding to a conventional acrylic polyelectrolyte and to a peptide electrolyte in aqueous solution, demonstrating alternate modes of self assembly of photoactive chromophores either in hypercoiled hydrophobic domains for folded polymer or in dye stacks for an ordered charge polymer (a helical peptide array)

(5) Investigation of the high potential quinone, chloranil, and its ability to induce reactions of organic electron donors via radical cations; in particular, further elucidation of the behavior of contact triplet radical ion pairs in non-polar media (intermediates in the 100 ns time scale).

(Refs 21 – 31)

Publications for the report period (DOE supported projects)

1. G. Jones, II, W.A. Haney, and X.T. Phan, "Photoaddition and Photoreduction of Chloranil with Arenes via Singlet and Triplet Excited Complexes: Effects of Irradiation Wavelength and Radical-ion Pair Spin Multiplicity," *J. Am. Chem. Soc.*, **110**, 1922 (1988).

2. G. Jones, II and S. Chatterjee, "Steric Control of Distance Parameters and the Yield of Charge Carriers in Photochemical Electron Transfer. Quenching of Eosin Triplet by Hindered Phenols," *J. Phys. Chem.*, **92**, 6862 (1988).

3. G. Jones, II and N. Mouli, "Long-lived Quinone-naphthalene Triplet Excited Complexes. Direct Measure of Rates of Proton Transfer Within Intimate Radical Ion Pairs," *J. Phys. Chem.*, **92**, 7174 (1988).

4. G. Jones, II, "Photochemistry and Photophysics of Charge-transfer Complexes," in "Photoinduced Electron Transfer," vol 1, M.A. Fox and M. Chanon, Ed., Elsevier Science Publishers, Amsterdam, 1989.

5. G. Jones, II and C. Weiss, "Dye Binding to Polytryptophan and Lysine-tryptophan Copolymer: Electron Transfer Quenching by Biopolymer Pendant Groups," in "Molecular Electronics - Biosensors and Biocomputers," F.T. Hong, Ed., Plenum Publishing Corp., New York (1989).

6. G. Jones, II, "2 + 2 Cycloaddition: Diverse Mechanisms of Valence Isomerization," in "Photochromic Materials and Systems," H. Durr and H. Bouas-Laurent, Eds., Elsevier Science Publishers, Amsterdam (1990).

7. G. Jones, II, C. Oh, and K. Goswami, "The Photochemistry of Triarylmethane Dyes Bound to Polyelectrolytes: Photoinduced Electron Transfer Involving Bound Dye Monomers and Triplets," *J. Photochem Photophys: A. Chemistry*, **57**, 65 (1991).

8. G. Jones, II, N. Mouli, and W.A. Haney, "Photoreduction of Chloranil by Benzhydrol and Related Compounds. Hydrogen Atom Abstraction vs. Sequential Electron-proton Transfer via Quinone Triplet Excited Complexes," *J. Am. Chem. Soc.*, submitted.

9. G. Jones, II and B. Huang, " Photoactive Peptides: Development of a Redox Catalytic Triad for Sulfide Oxidation Based on Poly(L)-histidine," *J. Phys. Chem.*, **96**, 9603 (1992).

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23. G. Jones, II, N. Mouli, W. A. Haney, W. R. Bergmark, "Photoreduction of Chloroanil by Benzhydrol and Related Compounds. Hydrogen Atom Abstraction vs Sequential Electron-proton Transfer via Quinone Triplet Radical Ion Pairs," *J. Am. Chem. Soc.*, **119**, 8788 (1997).

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28. G. Jones, II, L. N. Lu, H. Fu, C. W. Farahat, C. Oh, S. R. Greenfield, D. J. Gosztola, and M. R. Wasielewski, "Intramolecular Electron Transfer Across Amino Spacers in the Picosecond Time Regime. Charge-transfer Interaction through Peptide Bonds," *J. Phys. Chem.*, **103**, 572 (1999).

29. G. Jones, and J. A. C. Jimenez, Azole-linked Coumarin Dyes as Fluorescence Probes of Domain-Forming Polymers, 2nd Internet Symposium in Photochemistry, July-August, 1999 [www.photobiology.com/photo99index2.htm]; published *J. Photochem. Photobiol. Biol.*, (1999), in press.

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45. G. Jones, II, X. Zhou, V.I. Vullev, "Photoinduced Electron Transfer in α-helical Polypeptides: Dependence on Conformation and Electron Donor-acceptor Distance, **2**, 1080 (2003); contribution to Fred Lewis *Festschrift.*

46. G. Jones, II, V. Vullev, and H. Jiang, "Excimer Sensing", in Topics in Fluorescence Spectroscopy, vol 10; Eds., C. Geddes and J. Lakowitz, Academic Press, NewYork, 2004.

Selected Presentations of DOE-Supported Research

G. Jones, II and C. Weiss-Farahat, "Photoinduced Electron Transfer between Electroactive Groups on Polypeptide Chains," XIIIth IUPAC Symposium on Photochemistry, University of Warwick, Coventry, England, July, 1990.

G. Jones, II, "The Charge-shift Reaction in 9-Substituted Acridinium Ions," Gordon Conference on Electron Donor-Acceptor Interactions, Newport RI, August 15, 1994.

G. Jones, II, "Mechanistic Paradigms for Design of Photochemical Electron Transfer Systems," U. S.-Japan Workshop on Future Prospects for Photochemical Solar Energy Conversion," Kona, Hawaii, January 6-9, 1995

G. Jones, II, Electron transfer in synthetic proteins. Long range communication along alpha-helices, Minisymposium on Solid State Electron Transfer, Ecole Polytechnique Federale de Lausanne, Switzerland, February, 1999

G. Jones, II, and V. I. Vullev, Photosynthetic reaction center mimics. Photoinduced electron transfer in self-assembling polypeptide systems, Symposium on Novel Organic Structures and Mechanisms, Northeast Regional Meeting of the American Chemical Society, Potsdam, New,York, June, 1999

G. Jones, II, Electron transfer in synthetic proteins. Long range communication along alpha-helices, Minisymposium on Solid State Electron Transfer, Ecole Polytechnique Federale de Lausanne, Switzerland, February, 1999

G. Jones, II, and V. I. Vullev, Photosynthetic reaction center mimics. Photoinduced electron transfer in self-assembling polypeptide systems, Symposium on Novel Organic Structures and Mechanisms, Northeast Regional Meeting of the American Chemical Society, Potsdam, New,York, June, 1999

G. Jones, II, Bundles and threads: synthetic peptides engaged in photoinduced electron transfer, Gordon Research Conference, Connecticut College, New London CT, July, 1999

Selected contributed talk: G. Jones, II, and V. Vullev, Photosynthetic reaction center mimics. Special pair formation in synthetic polypeptide aggregates, Symposium on Chromophore Aggregation Phenomena, ACS National Meeting, New Orleans LA, August, 1999

Posters: 5th Chemical Congress of North America, Cancun, Mexico, November 11-15, 1997: Symposium on Supramolecular Structures: Characterization and Physical Aspects

G. Jones, II, and V. I. Vullev, "Photosynthetic Models Based on Helix Bundles" (# 1799)
G. Jones, II, and V. I. Vullev, "Peptide Aggregation and the Formation of Chromophore Pairs: Self Assembly of Photosynthetic Models" (# 1800)

Poster: 12th International Conference on Photochemical Conversion and Storage of Solar Energy, Berlin, Germany, August 9-14, 1998. Workshop: Artificial Photosynthesis

G. Jones, II, V. Vullev, and X. Zhou, "Photoinduced Electron Transfer in *de novo* Helix Bundles. A Reaction Center Model Based on Self Assembly of Peptide Chains" (5W 39)

Poster: 12th International Conference on Photochemical Conversion and Storage of Solar Energy, Berlin, Germany, August 9-14, 1998. Workshop: Artificial Photosynthesis

G. Jones, II, V. Vullev, and X. Zhou, "Photoinduced Electron Transfer in *de novo* Helix Bundles. A Reaction Center Model Based on Self Assembly of Peptide Chains" (5W 39)

Doctoral Thesis Research

The following theses were completed during the report period by students supported in part by DOE funds.

1. S. Chatterjee,

Photoreduction of Eosin by Substituted Phenols: Influences of Polymer Environment and Steric Interactions," Ph. D. Dissertation, 1988.

2. N. Mouli,
Quinone Sensitized Photooxidation of Aromatic Hydro- carbons and Arylmethanols: Influence of Substituents on Sequential Electron/Proton Transfer, Ph. D. Dissertation, 1988.

3. B. Huang
Photooxidation of Sulfides in Polypeptide Environments: Electrostatic Interactions and Neighboring Group Participation. Ph. D. Dissertation, 1992

4. Catie Weiss Farahat

Photophysical Properties and Photoinduced Electron Transfer for Modified Peptides Containing Tryptophan and Photosensitizers. Ph. D. Dissertation, 1993

5. Mohammad S. Farahat

Inter- and Intramolecular Electron Transfer Between Closely Associated Donors and Acceptors: Role of Intramolecular Reorganization. Ph.D. Dissertation, 1993

6. Churl Oh

The Structural and Photophysical Consequences of Dye Binding to Synthetic Polymers in Aqueous Solution. Ph. D. Dissertation, 1993

7. Zhiming Feng

Photochemical Properties of Eosin and Eosin Peptide Conjugates in the Microdomain of a Globular Polymer, Poly(N-vinyl-2-pyrrolidinone). Ph. D. Dissertation, 1994

8. Ning-Li Lu

Synthesis and Characterization of Photoactive Peptides Containing Tryptophan and Photosensitizers Ph. D Dissertation, 1995.

9. Ding-Xue Yan

Synthesis and Photochemical Study of Arylacridinium Derivatives. Ph.D. Dissertation, 1997.

10. Xiao-hua Qian

Organic Dyes as Photoprobes of the Microenvironment of Domain-forming Polymers. Ph. D., Boston University, 1998

12. Xiao-chun Wang

Photoinduced Electron Transfer and Ion Pairs. Ph. D. Dissertation, 1998.

13. Ding-xue Yan

Synthesis and Photochemical Properties of Arylacridinium Salts. Ph. D., Dissertation, 1997

14. Xiao-hua Qian

Organic Dyes as Photoprobes of the Microenvironment of Domain-forming Polymers.Ph. D. Dissertation, 1998

15. Xiao-chun Wang

Photoinduced Electron Transfer and Ion Pairs. Ph. D.Dissertation, 1998.

16. Valentine Vullev

Towards Artificial Photosynthesis: Photoinduced Multiple-Step Electron Transfer in Supramolecular Structures Based on Synthetic Polypeptides. Ph. D. Dissertation, 2001

17. Yue Sheng

Photoinduced Electron Transfer in Native Proteins and Domain Forming Polymers. Ph. D. dissertation, 2001

18. Oksana Klueva

Photophysical Properties of Organic Dyes Bound to Solid and Liquid Polymers. Ph. D. Dissertation, 2002

19. Xin Zhou

Photoactive Polypeptide Systems: Varied Mechanisms for Long Range Electron Transfer. Ph. D., Dissertation, 2002.

20. Satish Kumar

Electron Transfer Reactions in Electrostatic Polypeptide-Based Assemblies. Ph. D., Dissertation, 2003

21. Jingqui Hu

Electron Transfer Guest Arrays Incorporated in Domain Forming Aqueous Polymer Polypeptide, and Solid Host Media. Ph. D. Dissertation, 2004

Collaborations

Dr. Noriyuki Tanaka	Assistant Professor
(Visiting Scholar, B. U., 10/91-7/92)	Department of Chemistry
	Fukuoka Univ. of Education
	Fukuoka, Japan

Characterization of electron transfer products of tryptophan-containing peptides

Dr. Michael R. Wasielewski — (formerly) Division of Chemistry
Group Leader — Argonne National Laboratory
Sub-picosecond laser flash photolysis of reversible electron transfer in acridinium EDA systems

Dr. Hans van Willigen — Department of Chemistry
Professor of Chemistry — Univ. of Massachusetts, Boston
FT-ESR and CIDEP experiments on acridinium dyes and peptide conjugates

Dr. Frank Mari — Department of Chemistry
Assistant Professor of Chemistry — Florida Atlantic University
Conformational analysis of peptide and peptide conjugates by NMR spectroscopy

Dr. Mark Maroncelli — Department of Chemistry
Professor of Chemistry — Pennsylvania State University
Picosecond time resolved fluorescence methods

Dr. Laurence Ziegler — Department of Chemistry
Associate Professor of Chemistry — Boston University
Resonance Raman spectroscopic investigation of dye-polypeptide complexes

Dr. James A. Hamilton — Department of Biophysics
Professor of Biophysics — School of Medicine
Boston University
NMR spectroscopic techniques for peptide/protein ligand binding (domain mapping)

Dr. William R. Bergmark — Department of Chemistry
Professor of Chemistry — Ithaca College

Mechanistic studies of electron transfer photochemistry of quinones

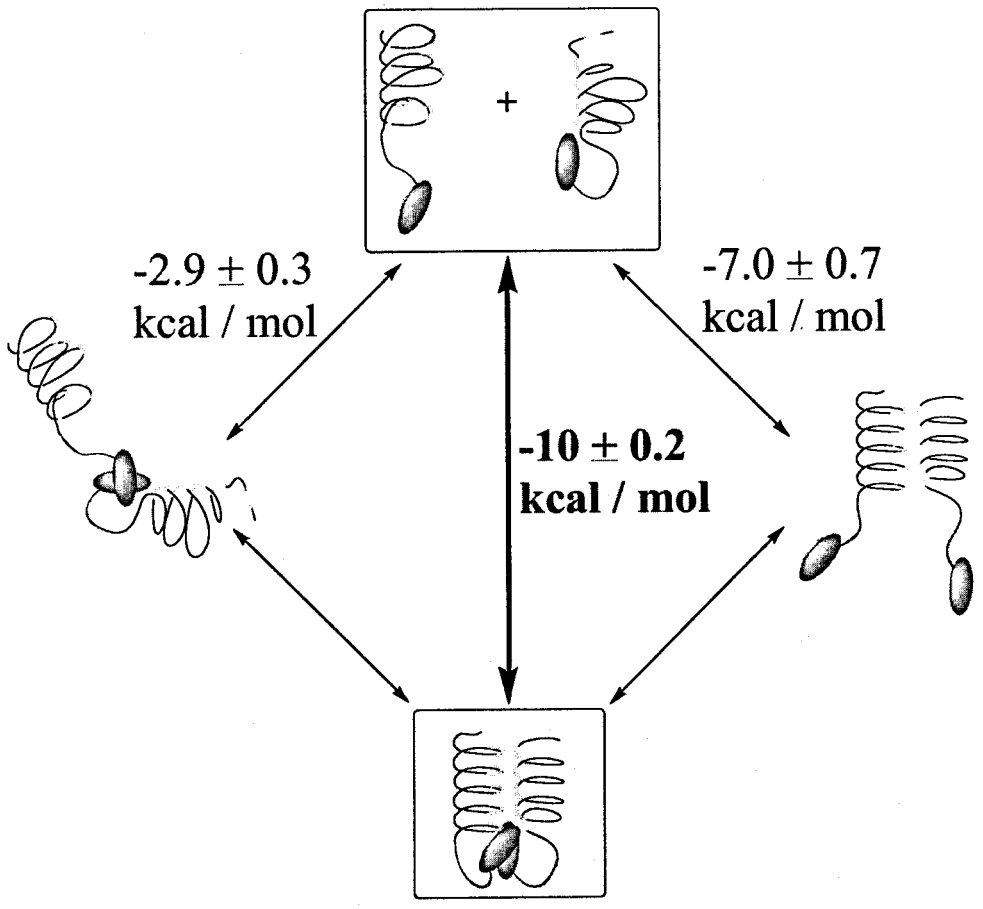

Figure 1

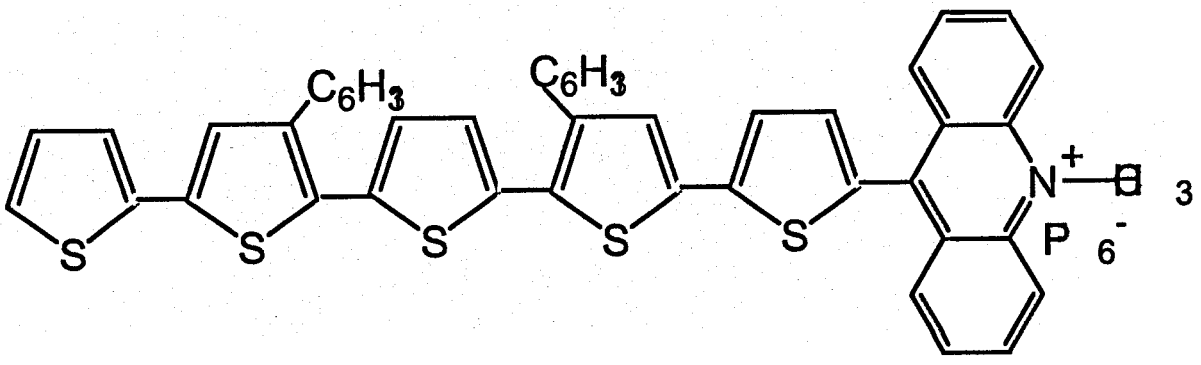

Figure 2